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The Photophysics of Poly(methylphenylphosphazene)

by

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The Photophysics of Poly(methylphenylphosphazene)

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ABSTRACT: The photophysical properties of poly(alkylarylphosphazenes), particularly poly(methylphenylphosphazene), PMPP, with a methyl and a phenyl group on the phosphazene phosphorous atom, have been investigated using absorption and emission spectroscopy, as well as laser flash photolysis. The fluorescence spectrum of PMPP shows a red-shifted emission (decay time greater than 1 nanosecond) with a maximum at 430 nm when excited at 270 nm in solvents of varying polarity. The absence of a strong solvent effect on the position and the structure of the fluorescence spectrum suggests that the emission is not due to a charge-transfer state, but originates from a significant geometry shift in the excited state. The triplet state of PMPP was identified by laser flash photolysis. The phosphorescence spectrum of PMPP indicates a triplet energy of 79 kcal/mol.

Introduction

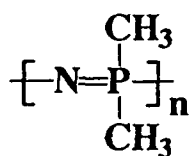
Since the synthesis of linear and soluble poly(organophosphazenes) by Allcock *et al*¹ in 1966, a great deal of work has been devoted to the preparation and characterization of phosphazene polymers suitable for use in many technological applications and containing different substituent groups.²⁻⁵ Minto *et al*⁶⁻¹³ carried out a series of investigations on the photochemical and photophysical behavior of poly(organophosphazenes) with heteroatoms attached directly to the phosphazene repeat unit in the backbone. Studies on the photochemistry and photophysics of similar poly(organophosphazenes) were also performed by Allcock¹⁴ and Webber.¹⁵ In 1980, we described¹⁶ a straightforward one-step condensation polymerization of a N-silylphosphoranimine (phosphinimine) resulting in the ultimate synthesis of a variety of poly(phosphazene) bearing alkyl and aryl groups connected to the parent polymer chain *via* attachment to phosphorous. This relatively new class of poly(phosphazenes) presents an interesting opportunity to investigate the photochemical and photophysical consequences of direct attachment of aromatic groups to the phosphorous atom on the phosphazene unit.

Recently, in a preliminary paper on the photochemical and photophysical

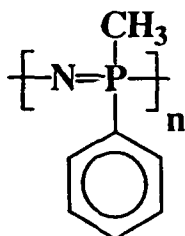
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behavior of this class of polymers, we reported¹⁷ that poly(methylphenylphosphazene), PMPP, gives a large Stokes' shifted emission when excited around 270 nm. In this paper we will present a more detailed account of our investigation on the photophysical properties of PMPP. Results for poly(dimethylphosphazene), PDMP, will be presented for a comparison as a non-aromatic bearing analog of PMPP. The photochemical behavior of PMPP will be discussed elsewhere.¹⁸



PDMP



PMPP

Experimental Section

Both PMPP and PDMP were prepared and purified by the method described earlier.¹⁶ All solvents were obtained from Burdick and Jackson and used as received. Absorption spectra were recorded on a Perkin-Elmer Lambda 6 UV-VIS spectrophotometer. Corrected fluorescence spectra were obtained on a Spex Fluorolog-2 spectrofluorometer with 3.5 nm bandpass excitation and emission slits using a rhodamine B solution as a quantum counter to generate the correction files. Phosphorescence spectra were recorded on a Spex Phosphorimeter model 1934D.

Fluorescence decay lifetimes were measured by a single-photon counting apparatus from Photochemical Research Associates International Inc. which is interfaced with a Digital VT240 computer. Transient absorption spectra were obtained with a laser flash photolysis apparatus based on an excimer laser excitation source (Lumonics HyperEx 440, 15 ns FWHM, nominal output at 248 nm was 80 mJ/pulse) and an Applied Photophysics xenon lamp/monochromator/PMT monitoring system as reported elsewhere.¹⁹

Results and Discussion

Figure 1 shows the UV spectrum of PMPP in dichloromethane. The absorption spectrum indicates the perturbation of the -P=N- backbone by the presence of the phenyl group resulting in a distinct absorption above 245 nm. For comparison, the UV spectrum of PDMP shown in Figure 1 exhibits little absorption above 245 nm due to the lack of an aromatic chromophore.

The emission and excitation spectra of PMPP in dichloromethane are shown in Figure 2. The most striking feature of the emission spectrum is a red-shifted emission with a maximum intensity at about 430 nm. This broad emission is at much lower energy than occurs for excimer formation²⁰⁻²³ between two phenyl

rings. For example, the excimer emission in polystyrene occurs at 335 nm.²⁴ Excitation at any wavelength within the main absorption band ($\lambda_{ex} < 280$ nm) of PMPP produced the same emission spectrum. The singlet energy (E_s) of PMPP is estimated to be 89 kcal/mol from the overlap of the emission and excitation spectra as shown in Figure 2. The fluorescence spectrum of a PDMP solution in dichloromethane is very weak and exhibits essentially no emission above 350 nm, which is not surprising considering its structure (Fig. 3). The low intensity emission which does occur for the PDMP solution could well be due to small amounts of an impurity. In general, the phosphorus-nitrogen bond distances in poly(phosphazenes) are shorter than expected for pure covalent σ bonds.²⁵ Interestingly, spectral effects normally associated with highly conjugated organic π -electron systems, such as the bathochromic ultraviolet shifts which accompany increased delocalization, are not found for PMPP. Thus, the phosphorus-nitrogen bond in poly(phosphazenes) differs somewhat from a covalent σ bond, and yet does not resemble the familiar σ - π bond of organic aromatic compounds.²⁵

The emission and excitation spectra of a cast film of PMPP are unusual in that the fluorescence spectrum is distinctly shifted to higher energy ($E_s = 97$ kcal/mol: estimated) with respect to that in solution (Fig. 4). Excited state

geometry restrictions in the film, which might be the reason for this shift, will be subsequently discussed in detail. The phosphorescence spectrum of PMPP in ether-tetrahydrofuran at 77 K gives a triplet energy (E_T) of 79 kcal/mol (Fig. 5), based on a shoulder at 360 nm that is assumed to be due to the 0,0 band of the phosphorescence emission. The phosphorescence lifetime is about 160 ms. The total emission spectrum of PMPP recorded at 77 K (not shown) resembled the phosphorescence spectrum: The emission from the singlet excited state is presumably buried under the phosphorescence emission.

The excitation and absorption spectra of PMPP (compare Figs. 1 and 2) are essentially identical, indicating that the origin of the emission with maximum at 430 nm is indeed initial absorption by the phosphazene unit, and that in the excited state the emission comes from the lowest energy level, regardless of the excitation wavelength. These results also indicate that the emission at 430 nm is not due to any impurity, but is rather an inherent property of the PMPP molecule. At first glance, the broad, red-shifted, structureless emission in Figure 2 is reminiscent of the intrapolymer excimer fluorescence associated with the aromatic moieties substituted on the polymer chain.²¹ For example, the fluorescence spectrum of polystyrene shows emission bands at about 280 and 335 nm, attributed to monomer

and excimer emission, respectively.²⁴ However, for PMPP the broad band is located at a very low energy precluding excimer fluorescence. In general,²² the peak of the excimer fluorescence from interacting phenyl type species is separated from the 0,0 band of the monomer fluorescence by $\sim 6000\text{ cm}^{-1}$. In PMPP, interestingly there is no emission observed corresponding to a phenyl monomer fluorescence (that should be at about 280 - 300 nm, if present). Further, the broad band in question differs significantly from the known²³ excimer fluorescence of alkyl-substituted phenyl groups whose peaks are located at $\sim 320\text{ nm}$. Even though the configuration of the excimer, if it existed in the present polymer, might well be different from that found in the carbon-based polymers, such a low energy excimer is unlikely. Also, in support of a single chromophore non-excimeric excited species for PMPP, the fluorescence decay of the emission at 420 nm is single exponential with a lifetime of 1.9 ns. The effect of concentration on the emission spectrum was also examined for polymer solutions in dichloromethane ranging from 0.03 mg/mL to 1.0 mg/mL. The intensity of the broad band is essentially independent of the polymer concentration, indicating that interpolymer excimer fluorescence does not occur either.

A plausible explanation for the emission at 430 nm might be a charge-

transfer state between the $-P=N-$ skeleton and the phenyl group. However, the position of the emission maximum does not shift when the solvent polarity is increased from dioxane, to dichloromethane, to 1:1 acetonitrile:dichloromethane (Fig. 6). This clearly indicates that the red-shifted emission with peak maximum at 430 nm is not due to an intrapolymer charge-transfer state. Furthermore, in view of the experimental finding that the intensity of the red-shifted emission is independent of the concentration of the polymer, we can also conclude that interpolymer charge-transfer states are not formed. Finally, we note that the emission of the cast film of PMPP is not due to phosphorescence, since the phosphorescence spectrum recorded in ether-tetrahydrofuran at 77 K (Fig. 5) has some structure, the 0,0 band appearing at 79 kcal/mol, and appears quite different from that recorded in film at room temperature (Fig. 4).

We propose that the red-shifted emission of PMPP with maximum at 430 nm in solution is due to a marked geometry shift in the excited state (compared to the ground state). Bearing this assumption in mind, we point out that the fluorescence spectra of PMPP in dichloromethane and in film (Figures 2 and 4) are entirely different: In the film at room temperature the fluorescence maximum is blue-shifted to 385 nm compared to 430 nm in solution. Apparently the restricted

polymer mobility at room temperature in the film ($T_g = 42^\circ\text{C}$) results in emission from an excited state with a geometry more like that of the ground state, i.e., from the vertical excited state, whereas, in solution, vibrational relaxation to a non-vertical excited state within the time scale of the emission process can occur with a concomitant red-shifted emission. In support of this supposition, the fluorescence spectrum of PMPP film above its T_g (i.e., at 80°C) shows a broad emission with a maximum between 385 and 430 nm (Fig. 7). Careful examination of the film spectrum at 80°C (Fig. 7a) indicates that the fluorescence of the PMPP film above T_g resembles a combination of the film and the solution fluorescence of PMPP (for a direct comparison, the fluorescence spectra of PMPP film at 25°C and solution are shown in Figures 7b and 7c, respectively). We might speculate that above the T_g of PMPP there is a mixture of excited species that emit from a range of relaxed and vertical geometries.

Fluorescence quenching studies provide an opportunity for examination of the polymer chain in terms of its accessibility to small quenching molecules. In our studies we have used carbon tetrachloride (CCl_4)²⁶⁻²⁹ as a simple quencher using the standard Stern-Volmer³⁰ equation

$$I_0/I_x = 1 + k_q\tau_0[X]$$

to evaluate the quenching rate constant, k_q , where I_0 and I_x are the relative fluorescence intensity in the absence and presence of a quencher, X, respectively, and τ_0 is the intrinsic lifetime of the excited state in the absence of the quencher. Non-linearity of Stern-Volmer plots can result from the presence of two or more species emitting at the same wavelength being quenched simultaneously, or else complex formation in the ground state: Such behavior was not observed in our system up to concentrations of 0.03 M CCl_4 . The bimolecular quenching rate constant, k_q , was $1.8 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$, typical of a dynamic quenching of a single excited state at a diffusion controlled rate.

In order to investigate the singlet-triplet intersystem crossing, the transient absorption spectrum (Fig. 8) of a nitrogen-saturated PMPP solution (dichloromethane) was recorded (laser flash photolysis - 248 nm excitation). The transient absorption spectrum is characterized by a peak around 360 nm with a single exponential decay time of 9.1 μs . In the presence of oxygen (air-saturated solvent) the transient decay time is much shorter ($\tau_T = 2.8 \mu\text{s}$) yielding a rate constant for oxygen quenching of about $1.8 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ suggesting that the

transient arises from either a radical species or a triplet state, both of which can be effectively quenched by oxygen. Addition of low concentrations of a typical triplet quencher, 1,3-cyclohexadiene (1×10^{-4} M or less), results in a uniform reduction in the lifetime of the transient species from PMPP in a nitrogen-saturated dichloromethane solution. A Stern-Volmer plot of the ratio of the transient lifetime before and after adding quencher *versus* the cyclohexadiene concentration is linear with a slope of $5.1 \times 10^4 \text{ M}^{-1}$ affording a quenching rate constant of $5.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. This is consistent with triplet quenching since cyclohexadiene has a triplet energy of 54 kcal/mol compared to 79 kcal/mol (deduced from the phosphorescence spectrum in Figure 5) for PMPP. In principle, the triplet state can also be generated directly by triplet sensitization experiments.¹⁹ Attempts to sensitize triplet state formation using acetophenone ($E_T = 74 \text{ kcal/mol}$) as a sensitizer (351 nm excitation) failed even in the presence of an excess of PMPP (1 mg/mL). This, of course, is not surprising since the triplet energy of PMPP is 79 kcal/mol. In order to avoid direct excitation of the polymer, we would need a sensitizer with a triplet energy equal to or preferably greater than 79 kcal/mol and which absorbs appreciably around 351 nm, the longest wavelength laser line available to us. Unfortunately, we are unaware of a long wavelength absorbing sensitizer with such a high triplet energy.

In summarizing the photophysical results, the energy levels and the radiative and radiationless deactivation processes of PMPP are presented in Figure 9 for reference. This scheme accounts for the red-shifted emission of PMPP with peak maximum near 430 nm. As stated previously, the red-shifted emission is attributed to a rapid geometry change occurring within the radiative lifetime of the polymer in fluid solution: The restricted mobility in the film prevents such a geometry shift, and hence leads to emission with a maximum at 385 nm. The fact that the absorption and excitation spectra of PMPP in solution coincide indicates that rapid radiationless deactivation processes occur from the S_1' excited state (unrelaxed state) to the S_1 excited state (relaxed state). Due to this rapid radiationless process, only emission from the relaxed excited S_1 state is observed in solution.

Conclusions

In summary, we have reported the photophysical behavior of a poly(alkyl-arylphosphazene). The fluorescence of the PMPP polymer is red-shifted with a maximum around 430 nm in fluid solution and 385 nm in film. The particularly large red-shift in the emission spectrum of PMPP is attributed to a significant geometry change in the relaxed singlet state. The singlet emission of PMPP with maximum at 430 nm in solution is readily quenched by CCl_4 . The triplet state of PMPP has been observed by laser flash photolysis and tentatively identified by triplet quenching experiments. The phosphorescence spectrum at 77 K indicates a high triplet energy (79 kcal/mol) for PMPP. The photochemical behavior of poly(methylphenylphosphazene), which culminates in a chain cleavage and/or cross-linking process, will be the subject of another paper.¹⁸

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Figure Captions

- Fig. 1. UV spectra of PMPP and PDMP in CH_2Cl_2 .
- Fig. 2. Emission and excitation spectra of PMPP in CH_2Cl_2 (λ_{ex} 270 nm; λ_{em} 430 nm). (Insert shows the expanded excitation spectrum).
- Fig. 3. Fluorescence spectrum of PDMP in CH_2Cl_2 (λ_{ex} 240 nm).
- Fig. 4. Emission and excitation spectra of PMPP film (λ_{ex} 270 nm; λ_{em} 380 nm).
- Fig. 5. Phosphorescence spectrum of PMPP in ether-THF at 77 K (λ_{ex} 270 nm) with a 300 μs delay.
- Fig. 6. Fluorescence spectra of PMPP in various solvents (λ_{ex} 270 nm): (a) dioxane; (b) CH_2Cl_2 ; and (c) 1:1 CH_3CN - CH_2Cl_2 mixture.
- Fig. 7. Fluorescence spectra of PMPP film at different temperatures and of solution (λ_{ex} 270 nm): (a) film at 80°C; (b) film at 25°C; and (c) in CH_2Cl_2 .
- Fig. 8. Triplet-triplet absorption spectra of PMPP in nitrogen-saturated CH_2Cl_2 at different time intervals after the flash (λ_{ex} 248 nm): (a) 2 μs after the flash; (b) 4 μs ; (c) 5 μs ; and (d) 10 μs .
- Fig. 9. Schematic representation of the energy levels and the radiative and nonradiative processes. The solid arrows indicate the radiative processes and the broken arrows indicate the nonradiative processes.

Fig. 1

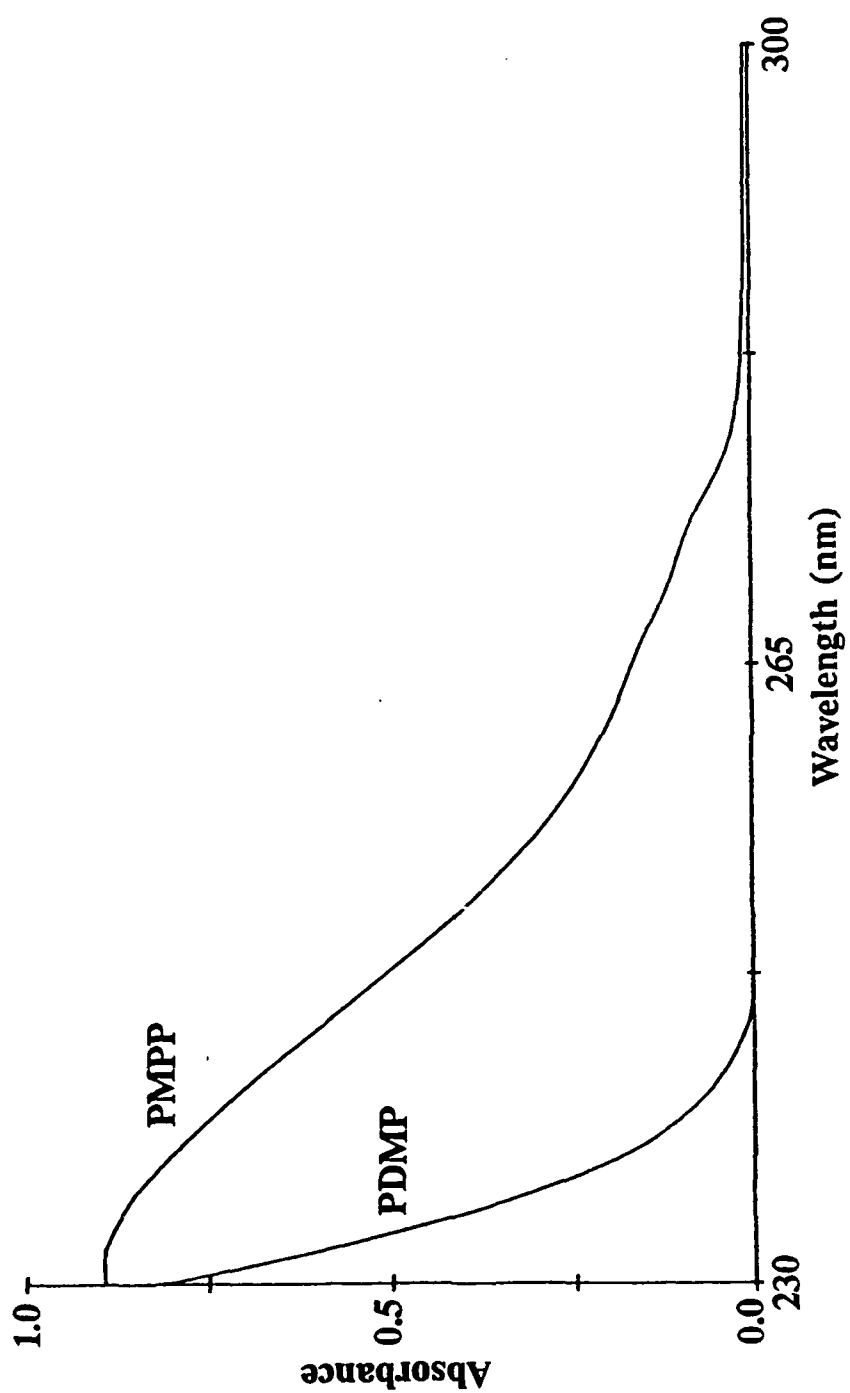


Fig. 2

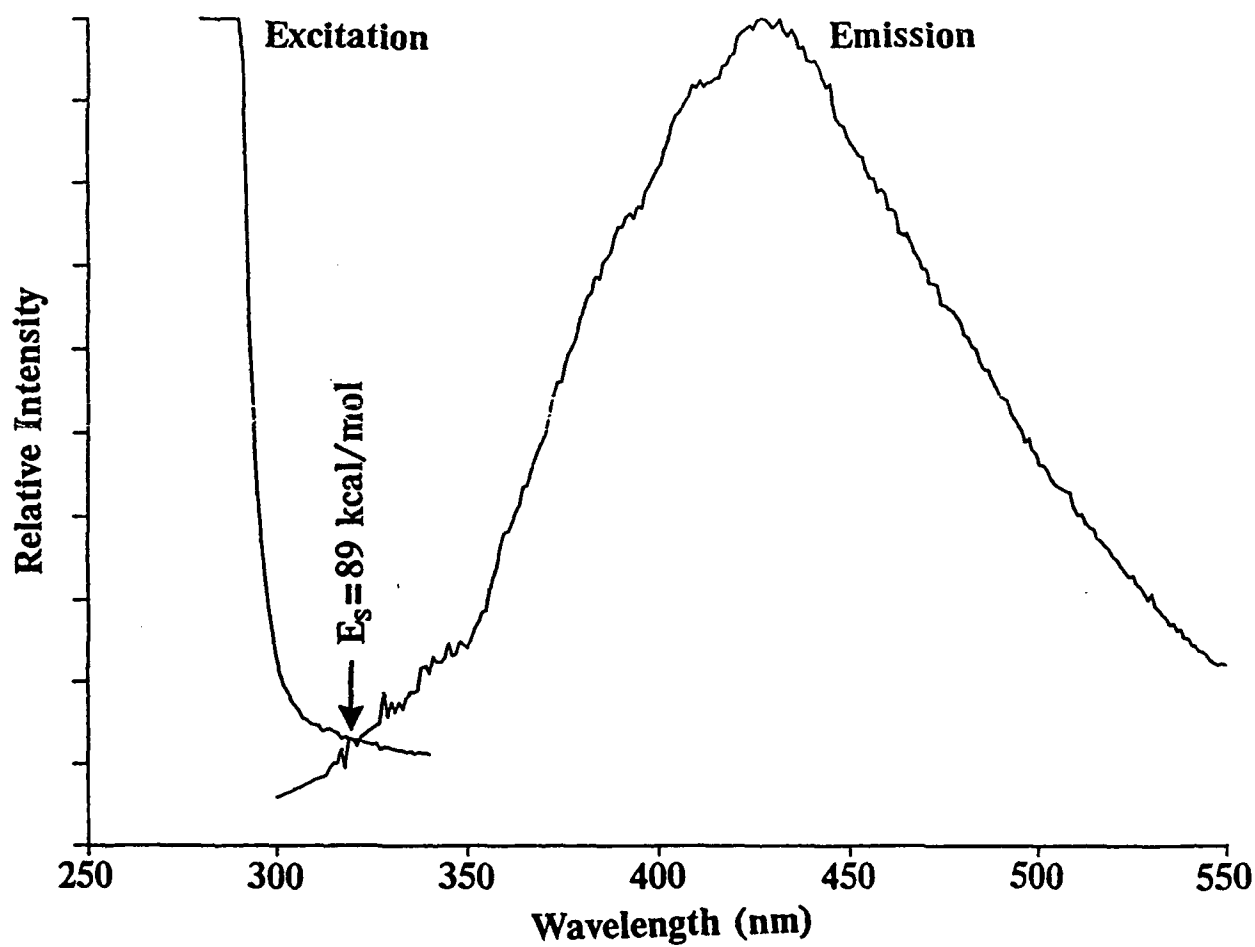
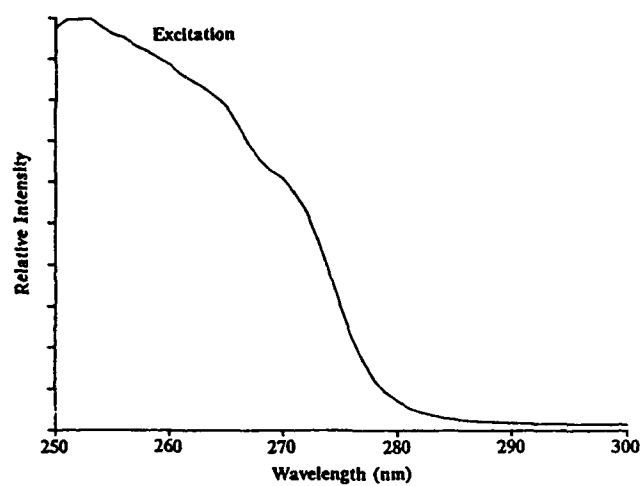


Fig. 3

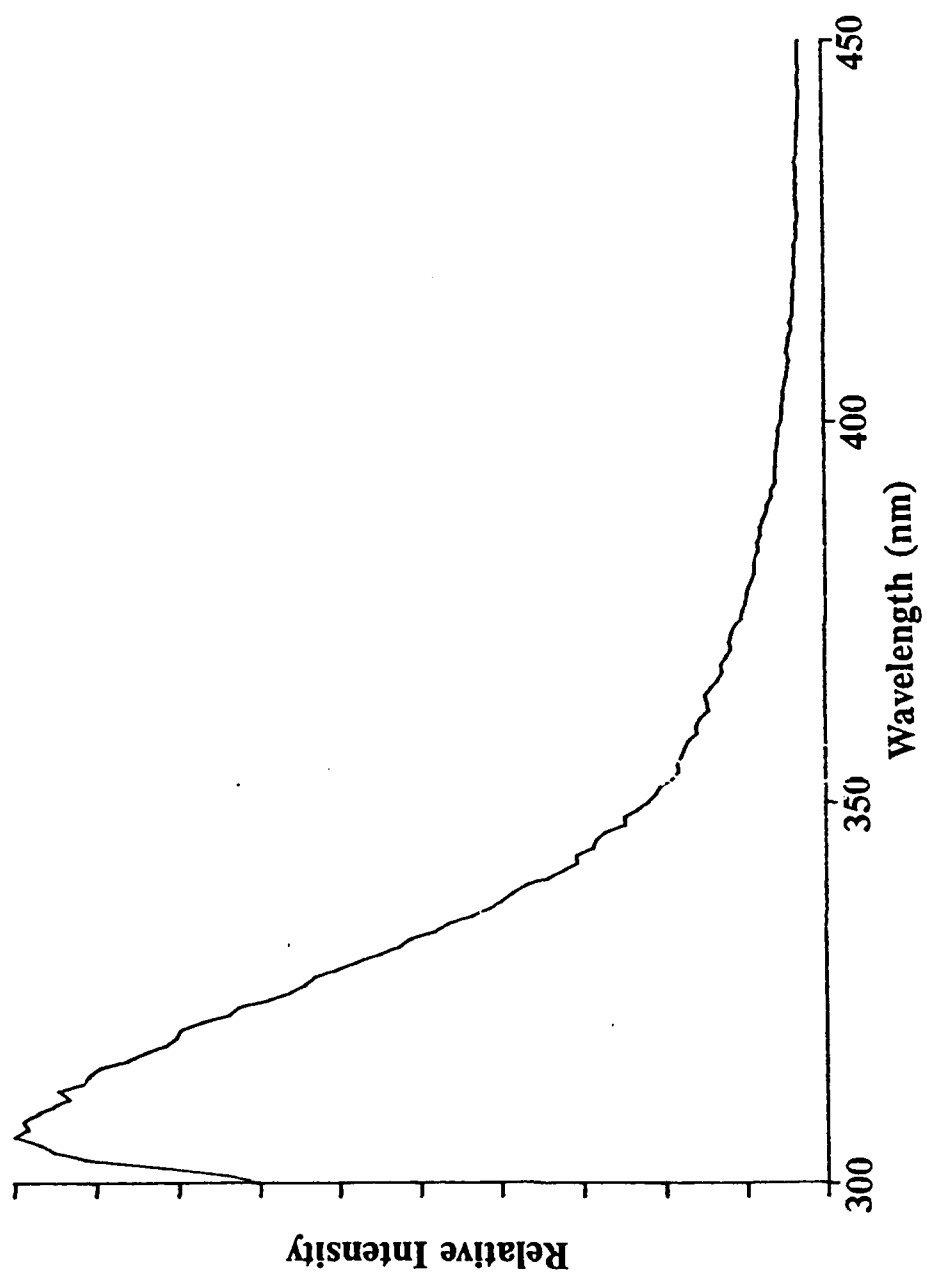


Fig. 4

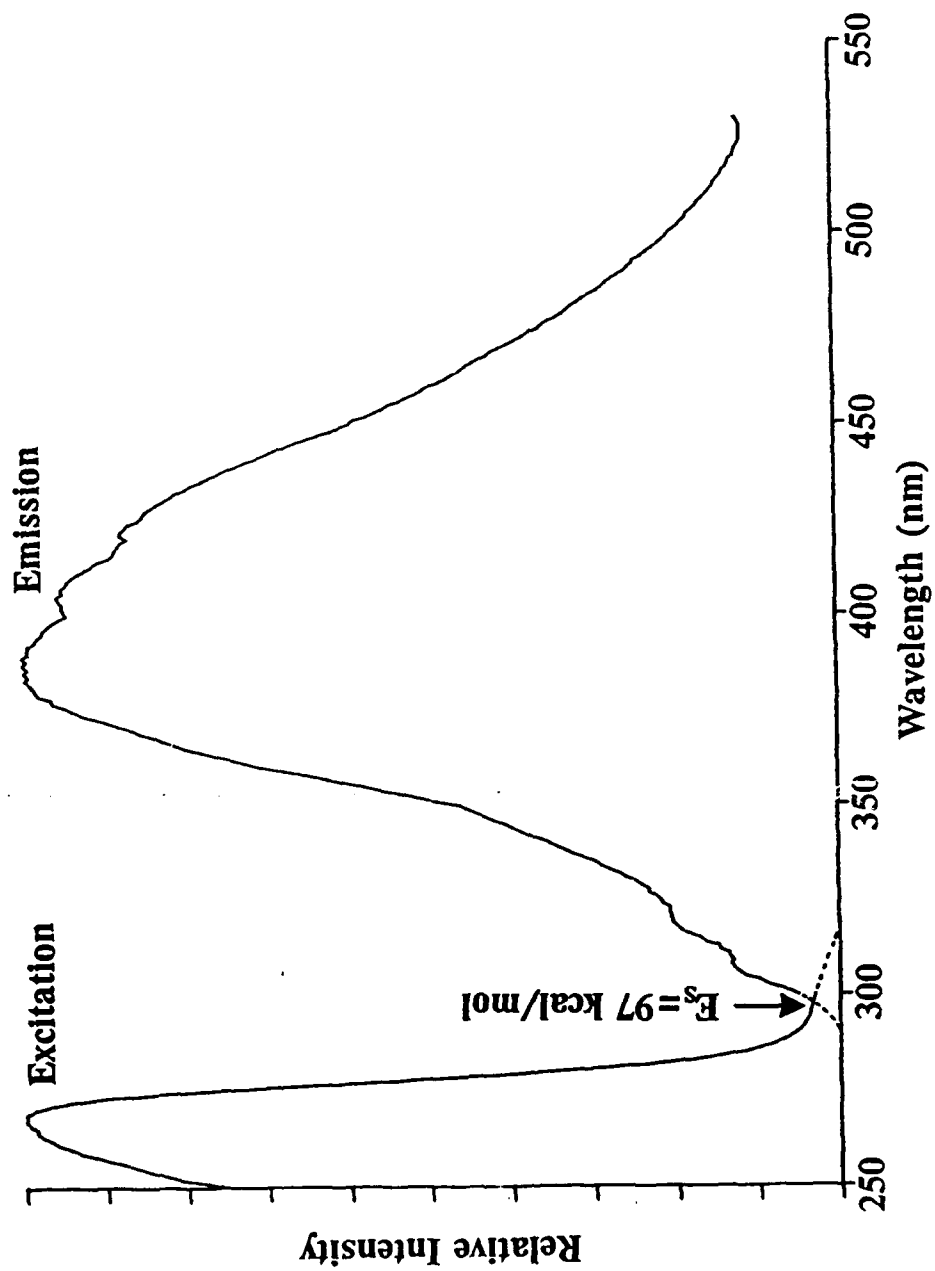


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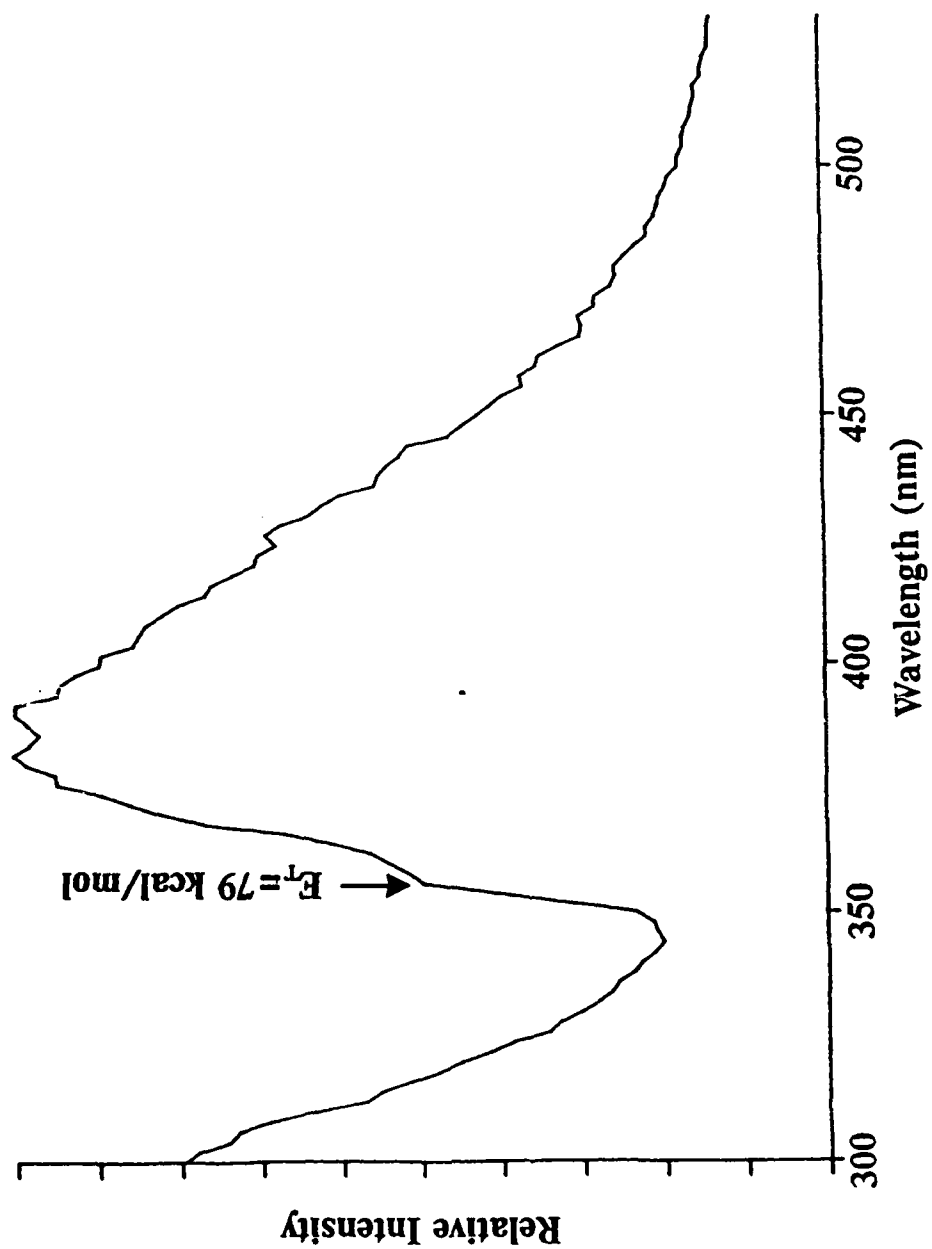


Fig. 6

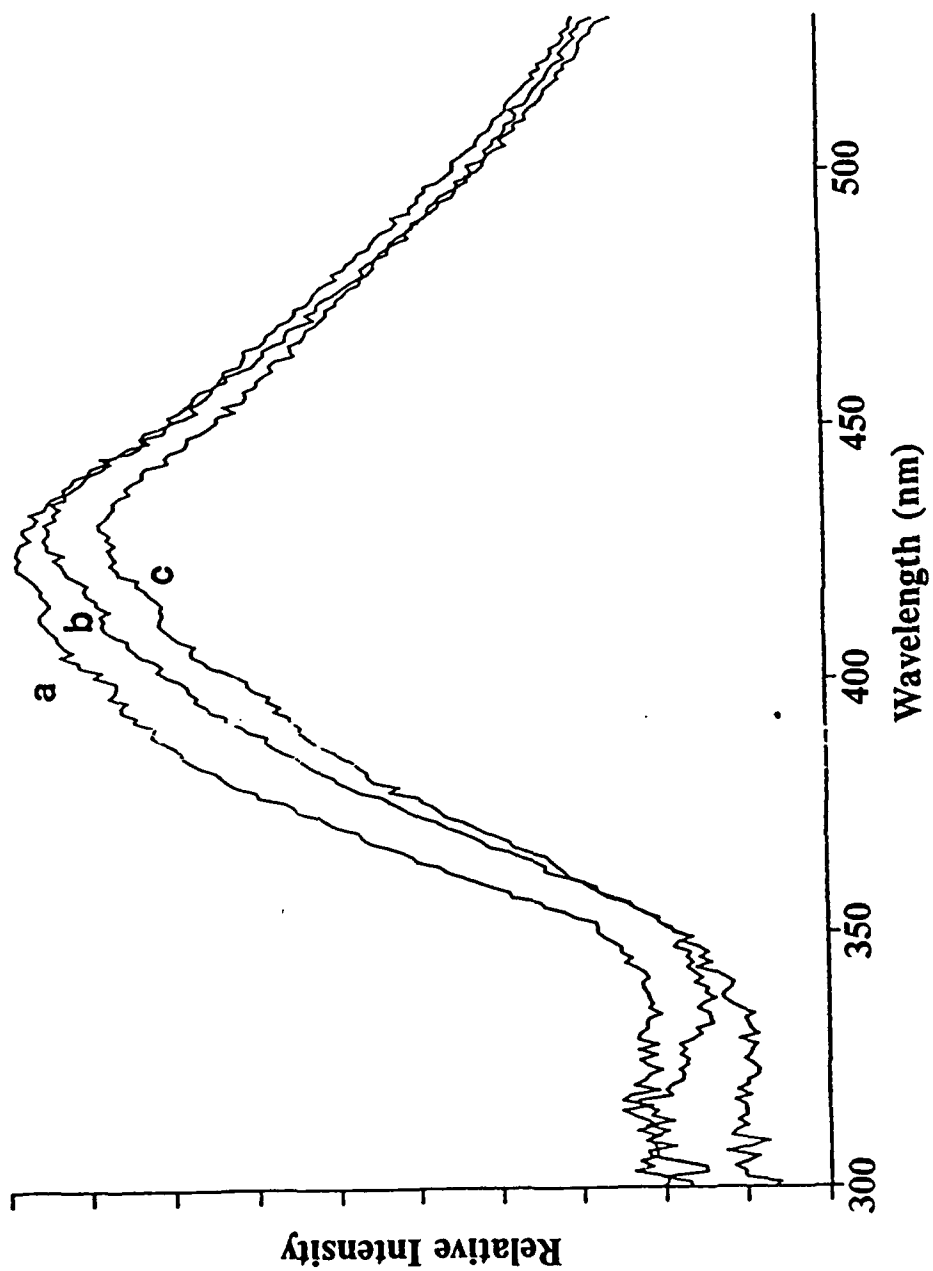


Fig. 7

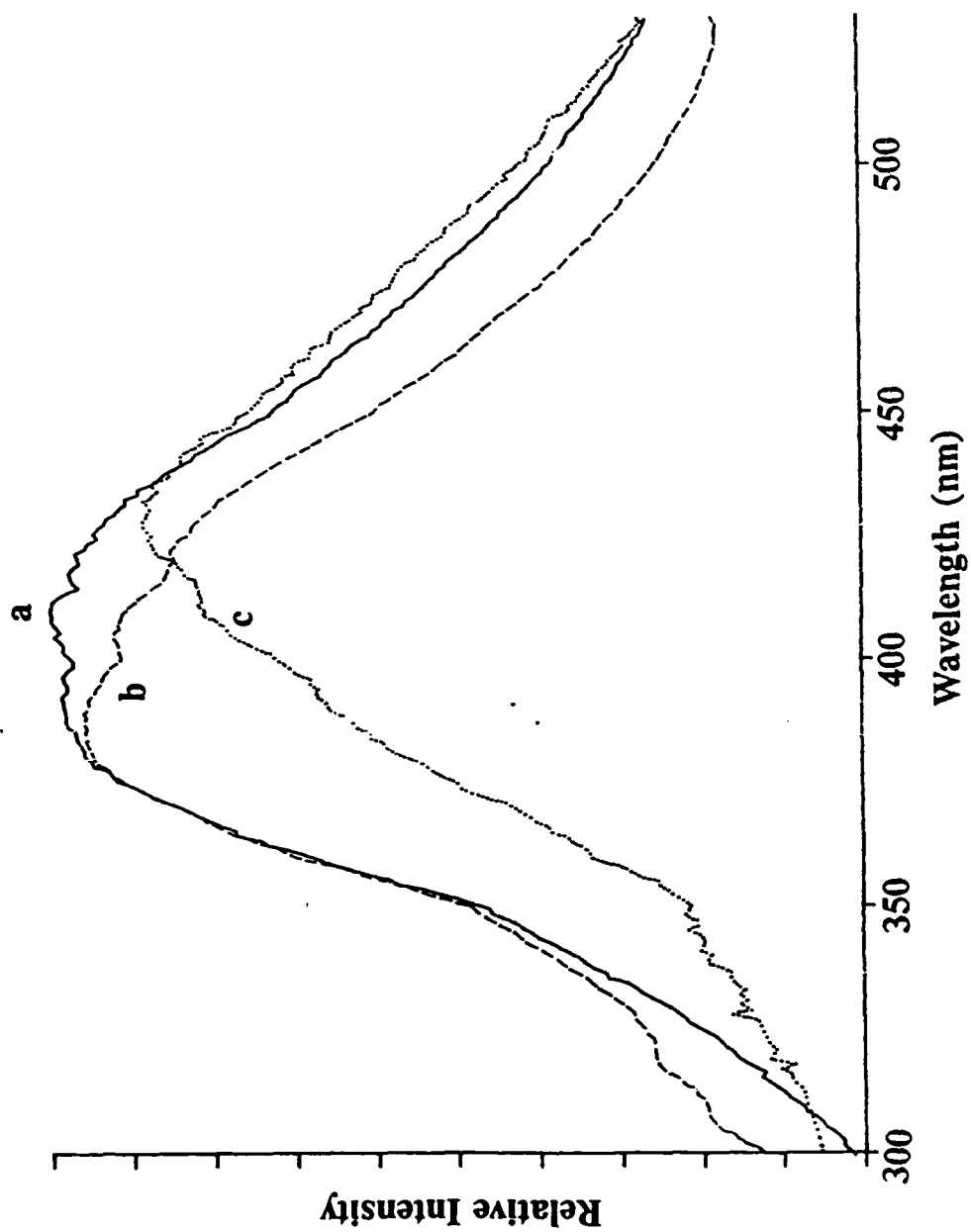


Fig. 8

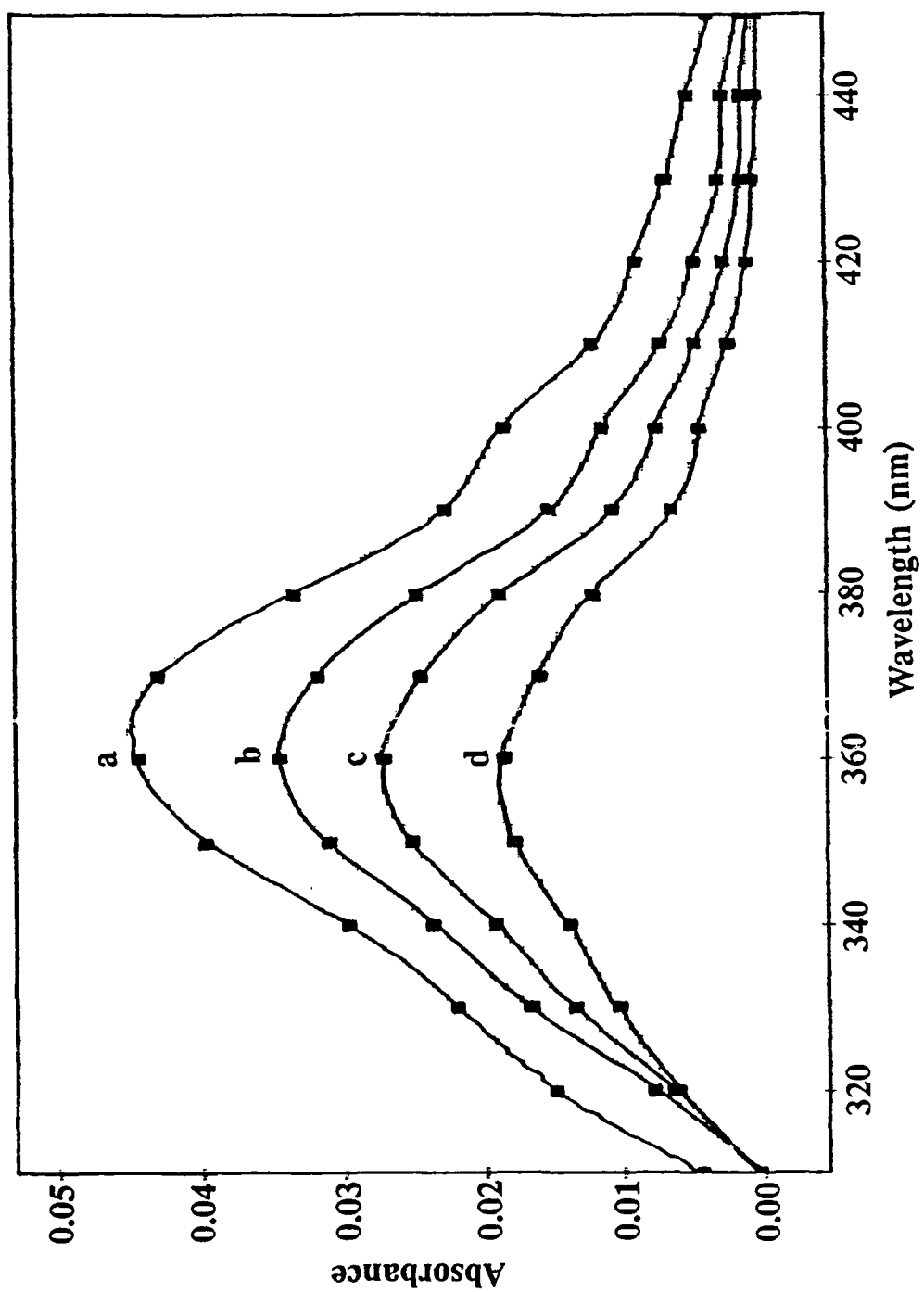


Fig. 9

